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## COMPUTATIONAL STUDIES OF METAL-METAL AND METAL-LIGAND INTERACTIONS

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# COMPUTATIONAL STUDIES OF METAL-METAL AND METAL-LIGAND INTERACTIONS

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Accurate calculations on the bond length, dipole moment and harmonic frequency of CO are presented, using large basis sets and high levels of electron correlation. The geometric structure, force constants and binding energies of  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$  are computed using large basis sets and high levels of electron correlation. The molecule  $\text{O}_4^+$  is studied, using large basis sets and high levels of electron correlation, including CASSCF, CASSI and CASPT2 methods. Binding energies, geometries and frequencies are computed. Symmetry breaking is a particular problem for the antisymmetric stretch, which is addressed using the CASSI method. The symmetry breaking problem in  $\text{O}_4^+$  has also been studied using the Brueckner coupled-cluster method. This gives results in good agreement with CASSI. A multi-region numerical integration scheme is investigated for use in Density Functional Calculations. This scheme is found to give comparable results to a widely used scheme based on the Euler-Maclaurin technique.

- “Bond length, dipole moment and harmonic frequency of CO”, L. A. Barnes, B. Liu and R. Lindh, J. Chem. Phys., **98**, 3972–3977, (1993)

A detailed comparison of some properties of CO is given, at the modified coupled-pair functional (MCPF), single and double excitation coupled-cluster (CCSD) and CCSD(T) levels of theory (including a perturbational estimate for connected triple excitations), using a variety of basis sets. With very large one-particle basis sets, the CCSD(T) method gives excellent results for the bond distance, dipole moment and harmonic frequency of CO. In a  $[6s\ 5p\ 4d\ 3f\ 2g\ 1h] + (1s\ 1p\ 1d)$  basis set, the bond distance is about  $0.005\ a_0$  too large, the dipole moment about 0.005 a.u. too small and the frequency about  $6\ \text{cm}^{-1}$  too small, when compared with experimental results.

- “Structure and energetics of  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$ ”, L. A. Barnes, B. Liu and R. Lindh, J. Chem. Phys., **98**, 3978–3989, (1993)

The geometric structure of  $\text{Cr}(\text{CO})_6$  is optimized at the modified coupled-pair functional (MCPF), single and double excitation coupled-cluster (CCSD) and CCSD(T) levels of theory (including a perturbational estimate for connected triple excitations), and the force constants for the totally symmetric representation are determined. The geometry of  $\text{Cr}(\text{CO})_5$  is partially optimized at the MCPF, CCSD and CCSD(T) levels of theory. Comparison with experimental data shows that the CCSD(T) method gives the best

results for the structures and force constants, and that remaining errors are probably due to deficiencies in the one-particle basis sets used for CO. A detailed comparison of the properties of free CO is therefore given, at both the MCPF and CCSD/CCSD(T) levels of treatment, using a variety of basis sets. With very large one-particle basis sets, the CCSD(T) method gives excellent results for the bond distance, dipole moment and harmonic frequency of free CO. The total binding energies of  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$  are also determined at the MCPF, CCSD and CCSD(T) levels of theory. The CCSD(T) method gives a much larger total binding energy than either the MCPF or CCSD methods. An analysis of the basis set superposition error (BSSE) at the MCPF level of treatment points out limitations in the one-particle basis used here and in a previous study. Calculations using larger basis sets reduce the BSSE, but the total binding energy of  $\text{Cr}(\text{CO})_6$  is still significantly smaller than the experimental value, although the first CO bond dissociation energy of  $\text{Cr}(\text{CO})_6$  is well described. An investigation of  $3s3p$  correlation reveals only a small effect. The remaining discrepancy between the experimental and theoretical total binding energy of  $\text{Cr}(\text{CO})_6$  is probably due to limitations in the one-particle basis, rather than limitations in the correlation treatment. In particular an additional  $d$  function and an  $f$  function on each C and O are needed to obtain quantitative results. This is underscored by the fact that

even using a very large primitive set (1042 primitive functions contracted to 300 basis functions), the superposition error for the total binding energy of  $\text{Cr}(\text{CO})_6$  is 22 kcal/mol at the MCPF level of treatment.

- “The fraternal twins of quartet  $\text{O}_4^+$ ”, R. Lindh and L. A. Barnes, J. Chem. Phys., **100**, 224–237, (1994)

Eleven stationary geometries of quartet  $\text{O}_4^+$  have been studied by *ab initio* methods. The geometries were optimized at the CASSCF level of theory and the energies were calculated by the CASPT2 method, using DZP, TZ2P, ANO[5s4p2d] and ANO[6s5p3d2f] basis sets. The rectangular and *trans*-planar structures are found to be the most stable, with an energy barrier to conversion between the two at the threshold of dissociation. Both have a delocalized hole and are stable relative to separated  $\text{O}_2$  and  $\text{O}_2^+$  by 11.0 and 11.5 kcal/mol for the rectangular and the *trans*-planar structure, respectively, compared with the experimentally deduced energy in the range of 9.2 to 10.8 kcal/mol. The adiabatic ionization potentials of  $\text{O}_4$  and  $\text{O}_2$  are computed to be 11.67 and 12.21 eV, while experimental values are 11.66 and 12.07 eV, respectively. The vibrational frequencies have been computed for all degrees of freedom at the CASSCF level of theory. Symmetry breaking is found to be a particular problem in the computation of the antisymmetric stretch frequency for the delocalized structures at the CASSCF level of theory. Attempts to

rectify these problems using the RASSCF method leads to additional difficulties, but further analysis yields insight into the symmetry breaking and problems with earlier calculations. Finally, a non-orthogonal CI calculation based on the interaction of localized CASSCF wavefunctions using the CASSI method leads to a balanced treatment of the antisymmetric stretch which is free from symmetry breaking. The study explains the four most prominent absorption frequencies observed in the partially unassigned IR spectrum of  $O_4^+$  isolated in solid neon as the antisymmetric OO-stretch, and the combination band of the symmetric and antisymmetric OO-stretch of *both* the rectangular and *trans*-planar structures.

- “Symmetry Breaking in  $O_4^+$ : an application of the Brueckner Coupled Cluster Method”, L. A. Barnes and R. Lindh, Chem. Phys. Lett., **223**, 207, (1994)

A recent calculation of the antisymmetric stretch frequency for the rectangular structure of quartet  $O_4^+$  using the QCISD(T) method gave a value of  $3710\text{ cm}^{-1}$ . This anomalous frequency is shown to be a consequence of symmetry breaking effects, which occur even though the QCISD(T) solution derived from a delocalized SCF reference function lies energetically well below the two localized (symmetry-broken) solutions at the equilibrium geometry. The symmetry breaking is *almost* eliminated at the CCSD level of theory, but the small remaining symmetry breaking effects are magnified at the CCSD(T)

level of theory so that the antisymmetric stretch frequency is still significantly in error. The use Brueckner coupled cluster method, however, leads to a symmetrical solution which is free of symmetry breaking effects, with an antisymmetric stretch frequency of  $1322\text{ cm}^{-1}$ , in good agreement with our earlier calculations using the CASSCF/CASSI method.

- “A multi-region integration scheme”, L. A. Barnes, work in progress (to be published)

In this preliminary report, a multi-region radial integration is compared to the recently proposed method due to Handy *et al.*. Preliminary results for small systems indicate that the new integration scheme is generally comparable to and sometimes better than that of Handy *et al.*, although this conclusion is by no means firm. Work for larger systems is continuing.



The following papers resulted from this research activity:

- (1) L.A. Barnes, B. Liu, and R. Lindh, "*Bond Length, dipole moment and harmonic frequency of CO*," J. Chem. Phys., **98**, 3972--3977, (1993).
- (2) L.A. Barnes, B. Liu, and R. Lindh, "*Structure and energetics of  $\text{Cr}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_5$* ," J. Chem. Phys., **98**, 3978--3989, (1993).
- (3) Lindh and L.A. Barnes, "*The Fraternal Twins of Quartet  $\text{O}_4^+$* ," J. Chem. Phys. **100**, 1, 224-237, (1994).
- (4) L.A. Barnes and R. Lindh, "*Symmetry Breaking in  $\text{O}_4^+$ : an Application of the Brueckner Coupled Cluster Method*," Chem. Phys. Lett., **223**, 207, (1994).
- (5) L.A. Barnes, "*A Multi-Region Integration Scheme*," to be published.

Papers (3) to (5) were not included in earlier reports submitted under this Cooperative Agreement and are attached to this final technical report.

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